8.2 Motion in two and more dimensions

Key points (a) The separation of variables technique can be used to solve the Schrödinger equation in multiple dimensions. The energies of a particle constrained to move in two or three dimensions are quantized. (b) Degeneracy occurs when different wavefunctions correspond to the same energy. Many of the states of a particle in a square or cubic box are degenerate.

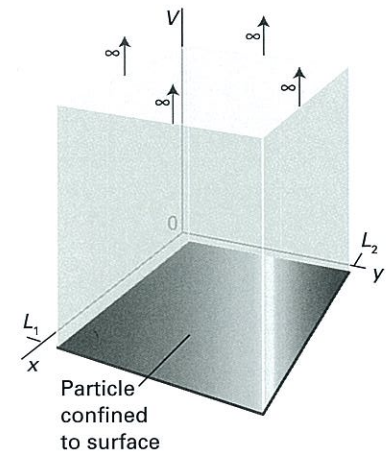

Fig. 8.5 A two-dimensional square well. The particle is confined to the plane bounded by impenetrable walls. As soon as it touches the walls, its potential energy rises to infinity.

Next, we consider a two-dimensional version of the particle in a box. Now the particle is confined to a rectangular surface of length L_1 in the x-direction and L_2 in the y-direction; the potential energy is zero everywhere except at the walls, where it is infinite (Fig. 8.5). The wavefunction is now a function of both x and y and the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=E\psi \tag{8.9}$$

We need to see how to solve this partial differential equation, a differential equation in more than one variable.

(a) Separation of variables

Some partial differential equations can be simplified by the **separation of variables technique** (*Mathematical background 4* following this chapter), which divides the equation into two or more ordinary differential equations, one for each variable. An important application of this procedure, as we shall see, is the separation of the Schrödinger equation for the hydrogen atom into equations that describe the radial and angular variation of the wavefunction. The technique is particularly simple for a two-dimensional square well, as can be seen by testing whether a solution of eqn 8.9 can be found by writing the wavefunction as a product of functions, one depending only on x and the other only on y:

$$\psi(x,y)=X(x)Y(y)$$

Separation of variables

With this substitution, we show in the following *Justification* that eqn 8.9 separates into two ordinary differential equations, one for each coordinate:

$$-\frac{\hbar^2}{2m}\frac{d^2X}{dx^2}=E_XX \qquad -\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2}=E_YY \qquad E=E_X+E_Y \tag{8.10}$$

The quantity E_X is the energy associated with the motion of the particle parallel to the x-axis, and likewise for E_Y and motion parallel to the y-axis. Similarly, $X(x)$ is the wavefunction associated with the particle's freedom to move parallel to the x-axis and likewise for $Y(y)$ and motion parallel to the y-axis.

Justification 8.2 *The separation of variables technique applied to the particle in a two-dimensional box*

We follow the procedure in *Mathematical background 4* and apply it to eqn 8.9. The first step in the justification of the separability of the wavefunction into the product of two functions X and Y is to note that, because X is independent of y and Y is independent of x, we can write

$$\frac{\partial^2\psi}{\partial x^2}=\frac{\partial^2XY}{\partial x^2}=Y\frac{d^2X}{dx^2} \qquad \frac{\partial^2\psi}{\partial y^2}=\frac{\partial^2XY}{\partial y^2}=X\frac{d^2Y}{dy^2}$$

Then eqn 8.9 becomes

$$-\frac{\hbar^2}{2m}\left(Y\frac{d^2X}{dx^2}+X\frac{d^2Y}{dy^2}\right)=EXY$$

When both sides are divided by XY, we can rearrange the resulting equation into

$$\frac{1}{X}\frac{d^2X}{dx^2}+\frac{1}{Y}\frac{d^2Y}{dy^2}=-\frac{2mE}{\hbar^2}$$

The first term on the left is independent of y, so if y is varied only the second term can change. However, the sum of these two terms is a constant given by the right-hand side of the equation; therefore, even the second term cannot change when y is changed. In other words, the second term is a constant. By a similar argument, the first term is a constant when x changes. If we write these two constants as $-2mE_Y/\hbar^2$ and $-2mE_X/\hbar^2$ (because that captures the form of the original equation), we can write

$$\frac{1}{X}\frac{d^2X}{dx^2}=-\frac{2mE_X}{\hbar^2} \qquad \frac{1}{Y}\frac{d^2Y}{dy^2}=-\frac{2mE_Y}{\hbar^2}$$

Because the sum of the terms on the left of each equation is equal to $-2mE/\hbar^2$ it follows that $E_X+E_Y=E$. These two equations rearrange into the two ordinary (that is, single variable) differential equations in eqn 8.10.

Each of the two ordinary differential equations in eqn 8.10 is the same as the one-dimensional square-well Schrödinger equation. We can therefore adapt the results in eqn 8.4 without further calculation:

$$X_{n_1}(x)=\left(\frac{2}{L_1}\right)^{1/2}\sin\frac{n_1\pi x}{L_1} \qquad Y_{n_2}(y)=\left(\frac{2}{L_2}\right)^{1/2}\sin\frac{n_2\pi y}{L_2}$$

Then, because $\psi=XY$ and $E=E_X+E_Y$, we obtain

Wavefunctions and energies of a particle in a two-dimensional box

$$\psi_{n_1,n_2}(x,y)=\frac{2}{(L_1L_2)^{1/2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2} \qquad (8.11a)$$

$$E_{n_1,n_2}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}\right)\frac{h^2}{8m} \qquad 0\le x\le L_1,\ 0\le y\le L_2$$

with the quantum numbers taking the values $n_1=1, 2, \ldots$ and $n_2=1, 2, \ldots$ independently. Some of these functions are plotted in Fig. 8.6. They are the two-dimensional versions of the wavefunctions shown in Fig. 8.3. Note that two quantum numbers are needed in this two-dimensional problem.

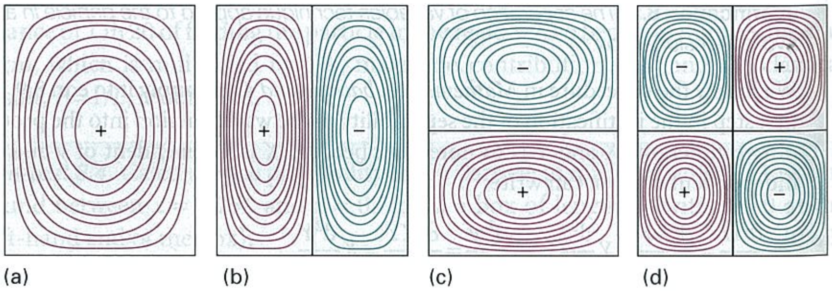

Fig. 8.6 The wavefunctions for a particle confined to a rectangular surface depicted as contours of equal amplitude. (a) $n_1=1$, $n_2=1$, the state of lowest energy, (b) $n_1=1$, $n_2=2$, (c) $n_1=2$, $n_2=1$, and (d) $n_1=2$, $n_2=2$.

interActivity Use mathematical software to generate three-dimensional plots of the functions in this illustration. Deduce a rule for the number of nodal lines in a wavefunction as a function of the values of n_x and n_y.

We treat a particle in a three-dimensional box in the same way. The wavefunctions have another factor (for the z-dependence), and the energy has an additional term in n_3^2/L_3^2. Solution of the Schrödinger equation by the separation of variables technique then gives

Wavefunctions and energies of a particle in a three-dimensional box

$$\psi_{n_1,n_2,n_3}(x,y,z)=\left(\frac{8}{L_1L_2L_3}\right)^{1/2}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}\sin\frac{n_3\pi z}{L_3}$$

$$E_{n_1,n_2,n_3}=\left(\frac{n_1^2}{L_1^2}+\frac{n_2^2}{L_2^2}+\frac{n_3^2}{L_3^2}\right)\frac{h^2}{8m}\qquad 0\le x\le L_1,\ 0\le y\le L_2,\ 0\le z\le L_3 \tag{8.11b}$$

with the quantum numbers taking the values $n_1 = 1, 2, \ldots, n_2 = 1, 2, \ldots$, and $n_3 = 1, 2, \ldots$, independently.

(b) Degeneracy

An interesting feature of the solutions for a particle in a two-dimensional box is obtained when the plane surface is square, with $L_1 = L_2 = L$. Then eqn 8.11a becomes

$$\psi_{n_1,n_2}(x,y)=\frac{2}{L}\sin\frac{n_1\pi x}{L}\sin\frac{n_2\pi y}{L}\qquad E_{n_1,n_2}=(n_1^2+n_2^2)\frac{h^2}{8mL^2} \tag{8.12}$$

Consider the cases $n_1 = 1, n_2 = 2$ and $n_1 = 2, n_2 = 1$:

$$\psi_{1,2}=\frac{2}{L}\sin\frac{\pi x}{L}\sin\frac{2\pi y}{L}\qquad E_{1,2}=\frac{5h^2}{8mL^2}$$

$$\psi_{2,1}=\frac{2}{L}\sin\frac{2\pi x}{L}\sin\frac{\pi y}{L}\qquad E_{2,1}=\frac{5h^2}{8mL^2}$$

We see that, although the wavefunctions are different, they are **degenerate**, meaning that they correspond to the same energy. In this case, in which there are two degenerate wavefunctions, we say that the energy level $5(h^2/8mL^2)$ is 'doubly degenerate'.

The occurrence of degeneracy is related to the symmetry of the system. Figure 8.7 shows contour diagrams of the two degenerate functions $\psi_{1,2}$ and $\psi_{2,1}$. As the box is square, we can convert one wavefunction into the other simply by rotating the plane by 90°. Interconversion by rotation through 90° is not possible when the plane is not square, and $\psi_{1,2}$ and $\psi_{2,1}$ are then not degenerate. Similar arguments account for the degeneracy of states in a cubic box. We shall see many other examples of degeneracy in the pages that follow (for instance, in the hydrogen atom), and all of them can be traced to the symmetry properties of the system (see Section 11.6).

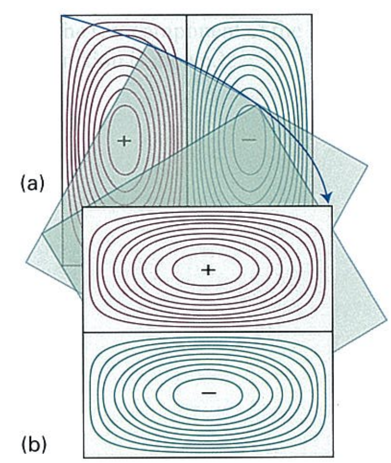

Fig. 8.7 The wavefunctions for a particle confined to a square surface. Note that one wavefunction can be converted into the other by a rotation of the box by 90°. The two functions correspond to the same energy. Degeneracy and symmetry are closely related.

IMPACT ON NANOSCIENCE

I8.1 Quantum dots

Nanoscience is the study of atomic and molecular assemblies with dimensions ranging from 1 nm to about 100 nm and nanotechnology is concerned with the incorporation of such assemblies into devices. The future economic impact of nanotechnology could be very significant. For example, increased demand for very small digital electronic devices has driven the design of ever smaller and more powerful microprocessors. However, there is an upper limit on the density of electronic circuits that can be incorporated into silicon-based chips with current fabrication technologies. As the ability to process data increases with the number of components in a chip, it follows that soon chips and the devices that use them will have to become bigger if processing